

**THE CHALLENGES OF HAZARD IDENTIFICATION AND CLASSIFICATION
OF INSOLUBLE METALS AND METAL SUBSTANCES FOR THE AQUATIC
ENVIRONMENT**

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Running head: challenges of hazard identification and classification of insoluble metals

ABSTRACT

Procedures for aquatic hazard identification of substances are currently being harmonized by the OECD. Such a system already exists in Europe where it is recognized that special consideration must be given to sparingly soluble metals and metal compounds (SSMMCs) because standard hazard testing procedures designed for organic chemicals do not accommodate the characteristics of SSMMCs. Current aquatic hazard identification procedures are based upon persistence, bioaccumulation and toxicity (PBT) measurements. Persistence measurements typically used for organic substances (biodegradation) do not apply to metals. Alternative measurements such as complexation and precipitation are more appropriate. Metal bioaccumulation is important in terms of nutritional sufficiency and potential food chain transfer and toxicity. Unlike organic substances, metal bioaccumulation potential cannot be estimated using log octanol-water partition coefficients. Further, bioaccumulation and bioconcentration factors are often inversely related to exposure concentration for most metals and organisms, and hence are not reliable predictors of chronic toxicity or food chain accumulation. Metal toxicity is due predominately to the free metal ion in solution. In order to assess the toxicity of SSMMCs, the rate and extent of transformation to a soluble form must be measured. Transformation can be assessed taking pH, particle size and /or surface area into consideration.

Key words: classification, metals, toxicity, persistence, bioaccumulation

INTRODUCTION

Procedures for aquatic hazard identification of organic and inorganic substances are currently being harmonized by the Organization for Economic Cooperation and Development (OECD) for the purpose of classifying market-place substances in terms of their potential hazard. Such a system already exists in Europe (EU, 1967; 1991) and is evolving in other countries (United States and Canada). One common theme in each of these systems is the use of persistence, bioaccumulation, and toxicity (PBT) measurements to estimate aquatic hazard. It is recognized within the OECD and European Union systems that special attention must be given to metal elements and sparingly soluble metals and metal compounds (SSMMCs). This recognition is based upon a common understanding that standard hazard testing procedures designed for soluble organic chemicals do not accommodate the special characteristics of SSMMCs. This paper briefly describes the challenges associated with hazard identification and classification of SSMMCs using PBT as the basis for the assessment.

PERSISTENCE

The concept associated with measuring persistence of substances in an environmental compartment (e.g., water, sediment, soil, air) is that the length of time the substance remains in a given compartment increases the possibility that the substance will accumulate over time and that exposure may increase with additional inputs. Persistence of organic substances is frequently assessed using biodegradation (CO_2 evolution / loss of dissolved organic carbon), hydrolysis and photolysis measurements. Loss of parent compound and conversion to a less toxic and persistent break down product is viewed as

desirable. Rapid degradation is interpreted as leading to a reduction in exposure. Complete mineralization to carbon dioxide and water is desirable.

While this is an appropriate approach for organics, the degradation tests used to assess persistence for organic substances do not apply to metals (Canada/European Union, 1996). The inability of metal elements to undergo degradation (especially biodegradation) is often translated to mean that metals are persistent. While all elements including carbon are persistent in the sense that the total mass present on the planet remains reasonably consistent, the intent of the biodegradation measurements for organic substances is to provide an estimate of the persistence of exposure. In that light, the appropriate measure for metals is an estimate of the persistency of the bioavailable metal species. Alternative measurements such as complexation, precipitation, and remineralization are more appropriate measures of persistency for metals than degradation. Complexation with dissolved organic carbon and suspended solids in surface waters and binding with iron and manganese oxides and sulfides in sediments are key processes controlling metal exposure in aquatic ecosystems. Significant differences in metal binding constants and solubility of metal hydroxides exist and range across more than 20 orders of magnitude (Figure 1) for different metal ions. These data are presented to indicate there are very large differences in metal bioavailability in surface waters and sediments and that these differences can be evaluated to assess persistency of metal species and exposure.

It is suggested that the water column is the appropriate place to focus an initial assessment of metals persistence since aquatic hazard assessment procedures are based upon toxicity tests designed, in principle, to evaluate the hazard of substances in typical

surface waters. A review of the existing literature shows both total and soluble fractions of most metal ions decline fairly rapidly following release in typical surface waters (DiToro and Paquin, 2000). This report reviews the persistence of total, and in some cases soluble metal, and supports the concept that an appropriate assessment of metal persistence in surface waters should include an assessment of the persistence of the bioavailable form of the metal species. The state-of-the-science has advanced to where this is now possible through the appropriate use of speciation models in conjunction with toxicity models (i.e., biotic ligand model). The basis for these models is a variety of field and laboratory experiments on the environmental persistence of metals. These experiments are briefly summarized below.

A variety of laboratory and field mesocosm experiments and designs were evaluated. Typical experiments use a large enclosure placed in a lake or beside an estuary. The experiments of Adler et al. (1980), Pilson et al. (1980), and Diamond et al. (1990) are briefly reviewed. Diamond et al. (1990) added a mixture of gamma-ray emitting metal isotopes into the water column and the progression of concentration in time was measured. The concentrations added were such that they increased the background concentration by no more than 10%, with the exception of mercury. The results of Diamond et al. (1990) for iron, cobalt, and zinc are shown in Figure 2. The total metal concentrations for two replicate experiments normalized to the initial concentration are shown versus the time from the initial introduction. The removal is approximately exponential in time. The lines are from a model calculation and half-lives for all the metals examined (arsenic, cesium, cobalt, iron, mercury, tin, and zinc) were less than 25 days.

A similar series of experiments (Adler et al., 1980) have been conducted at the MERL (Mesocosm Experimental Research Laboratory) facility at the University of Rhode Island, Graduate School of Oceanography (Pilson et al., 1980). The MERL mesocosms were somewhat larger (1.8 m by 5.5 m), contained seawater and sediments and were designed to mimic Narragansett Bay including mixing. The results for iron and cadmium are contrasted in that iron is removed rapidly (half-life = 3-5 days) whereas cadmium, which forms a soluble chloride complex in seawater, is not removed under these conditions over the length of the experiment (~45 days).

The half-life data from Diamond et al. (1990) show that the half-life for metals in the water column is directly related to the fraction of the metal that is sorbed to particles (Figure 3A). If c_d is the concentration of dissolved metal and c_p is the concentration of particulate metal (i.e., total metal minus dissolved metal concentration) then the particulate fraction is defined as $f_p = c_p / (c_d + c_p)$. For cesium, the particulate fraction is small and hence, the half-life is longer (i.e., 22 d). For cobalt, the particulate fraction is ~100% and the half-life is 5 d. The remaining metals have intermediate half-lives. Expressing the half-lives in relation to the particulate fraction reflects the sorption properties of each of the metals for suspended particles (algae, diatoms, soil particles) which provide the principal removal mechanism. It is important to note that even metals that are often considered to be somewhat soluble are removed from the water column relatively quickly. For the marine mesocosms, using the data of Diamond et al. (1990) and additional metals data from Adler et al. (1980), the half-lives are short, with the majority less than 10 days (Figure 3B).

Gächter (1979) conducted experiments in Lake Baldegg (Switzerland). The MELIMEX (MEtal LIMnological EXperiment) mesocosm experiment was quite large with a diameter of 12 m and a depth of 10 m. In this experiment, there was a continuous addition of metals for over one year. Cadmium, copper, lead, and zinc were tested. For all the metals except zinc, there was significant removal that continued throughout the year. Thus, the processes that removed the metal continued to operate for the duration of the experiment and were not just short-term effects. Data are shown for copper and zinc in Figure 4.

In addition to mesocosm experiments, whole-lake experiments have been carried out at the Experimental Lakes Area in Canada (Hesslein and Broecker 1980). Cobalt, cesium, iron, mercury, selenium, and zinc were tested. The half-lives, with the exception of selenium, were between 15 to 30 days in Lake # 224 (Figures 5 and 6).

Since the radioactive half-life of copper is very short, it cannot be used in either mesocosm or whole-lake experiments. However, copper sulfate is used as an algacide in lakes. Data from its use in Onondaga Lake and reported by Effler et al. (1980) was reviewed. Both the total and dissolved copper is removed from the water column fairly rapidly with half-lives less than 10 days (depicted in Figure 6).

The removal of dissolved metal from the water column is via two mechanisms. The first, and the least important in moderately deep systems, is via diffusion from the water column to the bottom sediments. The second is via the settling to the sediment of metal bound to particles. The dissolved metal initially present sorbs to the particles in the water column. These particles settle to the sediment. If no other process were operating,

a certain fraction of metal would be removed, but the rest would remain in the water column. The reason that removal continues is that new particles enter the water column. They are either created in the water column, such as algae, enter the water column from inflows, or are resuspended from the sediment. These new particles sorb additional metal and settle to the sediment, thereby continuing the process of metal removal from the water column.

Bioavailability of metals in sediment is an important part of site-specific risk assessments, but at present is not included in classification of substances. An approach for assessing metal bioavailability in sediments has been described by USEPA (2000).

In summary, data for lakes and estuaries have been presented that characterize and quantify metal persistence in natural surface waters. Similar data exist for streams (Thomann and Mueller, 1987) and for open oceans which are not summarized, but which are generally consistent with the conclusions drawn in this report. The principal conclusion of this review is that metal ions are not persistent in the water column of natural water bodies. Exceptions to this are cadmium in marine waters, and sodium in marine and freshwaters. Calcium, to a lesser extent might be considered an exception. Selenium and cobalt (marine waters) have somewhat longer half-lives, but overall are not excessively conservative. The data presented above for trace metals (aluminum, arsenic, cesium, chromium, copper, iron, lead, nickel, zinc, etc.) indicates that metal half-lives in surface waters vary but are generally from 22 days to less than 10 days depending on the fraction of the metal that is bound to particles.

BIOACCUMULATION

Bioaccumulation may be defined as the uptake and net accumulation of a chemical substance by an organism from its environment or diet. Relative to aquatic organisms, the ratio of the tissue concentration to the water concentration is termed the bioaccumulation factor (BAF). BAF estimates assume exposure from water or diet or both and are often derived from field data. Bioconcentration factors (BCFs) are used to define the ratio of the tissue concentration to the water concentration and assume water exposure and no dietary exposure. BCFs are typically derived in laboratory experiments and are often used in place of BAFs because the latter are not typically available. In performing aquatic hazard assessments for organic chemicals, bioaccumulation potential is typically assessed using BCFs. The assumptions associated with the use of estimated or measured BCFs are: (1) they are predictive of tissue residue concentrations and (2) larger BCFs indicate a greater potential for long term (chronic) effects and reflect a greater concern for trophic transfer of the substance.

The above assumptions are based on studies performed for the most part with non-polar organic chemicals that passively partition to lipids. For these organic substances, bioconcentration factors can be estimated by a measure of the octanol-water partition coefficient (K_{ow}). There is general recognition that large K_{ows} or BCFs provide evidence that a substance is “bioaccumulative.” There are important differences between organic substances and metals (defined as soluble metal in the water phase and total metal in the diet or tissue). It is recognized, that metals can be taken up from water and/or diet by aquatic organisms and stored in their tissues. This process of bioaccumulation occurs in all aquatic environments for both essential and non-essential

metals. While the process of bioaccumulation is important, the applicability of BCFs as an indicator of hazard has not been demonstrated and has been questioned. Experts convened at an international workshop in Brussels (Canada/European Union, 1996) and concluded that BCFs and BAFs are not useful indicators of hazard for metals. Recently, an in-depth review of the utility of BCFs for 12 metals was performed by Brix and DeForest (2000) and is briefly summarized in this paper.

It is well known that several metals are essential for various biological functions, such as enzymatic and metabolic reactions (Depledge and Rainbow, 1990; Goyer, 1996; Leland and Kuwabara, 1985). Metal bioaccumulation is an important process whereby aquatic organisms obtain these essential metals. Aquatic biota regulate their internal concentrations of essential metals in three ways: active regulation, storage, or a combination of active regulation and storage. Active regulators are organisms that maintain stable tissue concentrations by excreting metal at rates comparable to the intake rate (Rainbow, 1988). Other biota store metals in detoxified forms, such as in inorganic granules or bound to metallothioneins (Brown, 1982; Rainbow, 1987). Most organisms actually use a combination of these two regulatory strategies. It should also be noted that non-essential metals are also often regulated to varying degrees because the mechanisms for regulating essential metals are not metal-specific (Phillips and Rainbow, 1989). In general, essential metals such as copper and zinc tend to be actively regulated by organisms such as decapod crustaceans, algae and fish. Conversely, organisms such as bivalve mollusks, barnacles, and aquatic insects tend to store these metals in detoxified forms. Non-essential metals, such as cadmium and lead, are typically stored in detoxified forms.

As a result of these metal regulatory processes, an inverse relationship exists between water concentrations of metals and the corresponding BCF. Thus at low water concentrations, organisms are actively accumulating essential metals (and often non-essential metals via the same uptake mechanisms) to meet their metabolic requirements. At higher water concentrations, organisms with active regulatory mechanisms are able to excrete excess metals or limit uptake (Figure 7). An extensive review of the literature demonstrates that this hypothesis is correct for both essential (Figure 8) and non-essential (Figure 9) metals for most organisms (Brix and DeForest, 2000).

As a consequence of aquatic organisms regulatory ability, metal concentrations in tissue measured across a range of water exposure concentrations are often quite similar. The corresponding BCFs will not be constant, but will be inversely related to exposure concentration (i.e., higher BCFs at lower exposure concentrations and lower BCFs at higher exposure concentrations). Consequently, an individual BCF provides little information on the bioaccumulation potential of a metal for most organisms. In summary, relative to metals (and in contrast to organic substances), one cannot assume that as the BCF or BAF becomes larger, the potential for hazard is greater.

The concept that BCFs or BAFs can be used as an indicator of long-term or chronic toxicity to aquatic organisms stems from the assumption that larger BCFs are indicative of higher tissue concentrations, which in turn result in direct or secondary poisoning. This concept is primarily relevant to organic chemicals with narcosis as the mode of toxic action. However, this relationship does not apply to all chemicals, including metals. In fact, some studies have shown that accumulated metal (whole body residue) may be poorly, or even negatively, correlated with toxicity. Organisms that tend

to bioaccumulate metals to high levels do so because they are able to store the metals in detoxified forms (i.e., in granules, or bound to metallothioneins) and not because they have large BCFs or BAFs. As a result, organisms with larger BCFs actually tend to be less sensitive. This is demonstrated in Figure 10 for cadmium where daphnids are known to be among the most sensitive organisms and insects among the least sensitive and yet, the BCFs are highest for insects and lowest for daphnids (USEPA, 1984). Consequently, the magnitude of a metal's BCF cannot be used as a predictor of chronic toxicity.

Secondary poisoning occurs when chemical concentrations in an organism reach levels that are toxic to organisms that feed on it. For organic substances, chemicals that are highly "bioaccumulative" or which biomagnify in food webs often are considered to have the greatest potential to cause secondary poisoning. Biomagnification is the process whereby a substance increases in concentration as it passes up two or more trophic levels in the food web. It has been reported that the classic concept of biomagnification and food chain poisoning, based primarily on chemicals such as DDT and PCBs (Eisler, 1986; Keith, 1996), does not apply to metals, although naturally occurring organo-metals may be an exception (Suedel et al., 1994). This may be explained in part by the limited bioavailability of the inorganic forms of metals in food and by the regulation of metals that occurs in both aquatic and terrestrial organisms. Site-specific data are available suggesting that some inorganic metal compounds may be instrumental in producing secondary poisoning, (Woodward et al., 1994). This occurrence is typically associated with elevated site-specific exposure levels and is not reflective of the inherent bioaccumulative nature of the metal substance.

Considering the above, we conclude that metal BCFs are not indicative of the potential for direct toxicity, that inorganic forms of metals do not biomagnify in food webs and that secondary poisoning attributed to metals is a function of site-specific exposure. Further, we conclude that bioconcentration factors are not an appropriate parameter for assessing the hazard potential of metals. This is consistent with the results of the Brussels Workshop (Canada/European Union, 1996).

TOXICITY

It is widely recognized that the toxicity of mono- and divalent metals is due predominately to the free metal ion in solution (estimated by soluble metal measurements). Most of the toxicity data available to date have been derived using soluble metal salts and these data are then used to characterize the toxicity of the metal itself. The assumption is that the dissolved metal ions in laboratory tests are completely dissolved and bioavailable. Application of these data to metal elements requires the further assumption that the metal will transform from the element to free metal ions and these free metal ions will be bioavailable to exert toxicity. This is not always the case. Recent advances in estimating the bioavailable fraction of metal in solution using the Biotic Ligand Model allows for more accurate predictions of toxicity under relevant environmental conditions (DiToro et al., In Press). Differences in pH, dissolved organic carbon, hardness and other water quality parameters can be accounted for in the model allowing predictions of bioavailability and toxicity in the field using laboratory data. At present, the model has been developed for copper and silver and is being expanded to other metals.

The acute and chronic toxicity of metals (cadmium, copper, nickel, lead, silver, zinc, etc.) have been measured with numerous species. The tests have been conducted with soluble metal salts and the results expressed in terms of the toxicity of the metal and not the salt. Data sets range from a few dozen tests for lead to nearly 1000 tests for copper. Toxicity characterization approaches (water quality criteria, risk assessments, and classification systems) are designed to select a concentration deemed to be protective of most species in the environment. These approaches may utilize a toxicity value for the most sensitive species in the data set, or in some cases, a toxicity value that is at or near the lower five percentile of all species tested (Stephan et al., 1985). Acute toxicity data are most often used for classification purposes. The toxicity of most dissolved metal salts to sensitive species lies in the range of 0.1 to 1000 $\mu\text{g/L}$ (Table 1). The data presented in Table 1 were derived for purposed of setting water quality criteria (USEPA, 1998), but serve to illustrate the range of acute and chronic toxicity values obtained for various metals for sensitive species.

OECD and European Union classification approaches as well as the United States and Canadian PBT prioritization approaches utilize a 1.0 mg/L cutoff value for identifying substances as highly toxic. Depending upon the regulatory system, other less severe designations also exist for substances with toxicity values in the 1-10 mg/L or 1-100 mg/L range. These cutoff values have been determined to provide discriminatory power among organic substances in order to identify substances with the greatest aquatic hazard. It is pointed out that these regulatory approaches were not specifically designed with metals and other inorganic substances in mind. Using a cutoff value of 1.0 mg/L would identify nearly all of the common soluble metal substances as highly toxic. This

approach provides little discrimination between metal compounds and indicates that aluminum and iron compounds present as great a hazard as do mercury and cadmium. Hence, this does not appear to be a useful approach for assessing the hazard of metal substances. It is pointed out that the acute toxicity of common soluble metal compounds span three orders of magnitude from approximately 1 µg/l to 1000 µg/L. An alternative approach for SSMMCs might utilize cutoff values across the range of 1 to 1000 or 1 to 100,000 µg/L.

In order to assess the acute aquatic toxicity of SSMMCs, the rate and extent of transformation of metal to a soluble form must be measured. While soluble metal salts will readily dissolve in water at low mg/L concentrations, transformation of insoluble metal substances to soluble forms (dissolution) is a function of several key factors including particle size, surface area, ionic strength, pH of the test solution, and duration of the test. A standard protocol for measuring transformation is currently being developed and tested (OECD, 2000). The purpose of establishing a standardized dissolution/transformation protocol is to provide a methodology that allows for a determination of whether or not an insoluble metal substance will transform and dissolve in water over a reasonable period of time to the extent that toxicity may occur.

CONCLUSIONS

Toxicity of a metal is due predominately to the free metal ion in solution. In order to assess the acute aquatic toxicity of SSMMCs the rate and extent of transformation of a metal element or insoluble metal compound to a soluble form must be measured. Transformation of insoluble metal substances to soluble forms is a function of

several key factors including particle size, surface area, and the pH of the test solution. A standard protocol for measuring transformation is currently being developed by the OECD. Persistence measurements typically used for organic substances (biodegradation) do not apply to metals. Alternative measurements such as complexation, precipitation, and mineral formation are more appropriate. Bioaccumulation of metals by aquatic organisms is an important process both for in terms of nutritional sufficiency and potential food chain transfer and toxicity. Unlike organic substances, bioaccumulation potential can not be estimated using log octanol-water partition coefficients (K_{ow}), bioaccumulation and bioconcentration factors (BAFs/BCFs) are often inversely related to exposure concentration, and BCFs and BAFs are not reliable predictors of concern for chronic toxicity or food chain accumulation. Potential concern for bioaccumulation of sparingly soluble metals and metal compounds by aquatic organisms should be assessed on a case by case basis.

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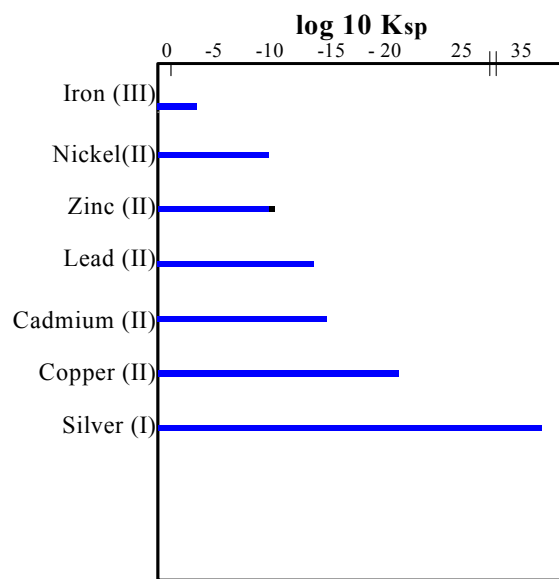
Table 1. Summary of acute and chronic toxicity data (US EPA water acute and chronic quality criteria values)

	Acute Toxicity	Chronic Toxicity
Metal (Soluble Salt)	(CMC) ¹	(CCC) ¹
Iron	---	1000
Arsenic	340	148
Zinc	120	120
Aluminum	750	87
Chromium III	570	74
Nickel	470	52
Cobalt	706	42
Chromium VI	16	11
Copper	14	9
Selenium	20	5
Lead	82	3.2
Cadmium	4.5	2.5
Mercury	1.7	0.91
Silver	0.92	0.12

¹ CMC = criterion maximum concentration which is the U.S. acute water quality criterion.
CCC = criterion continuous concentration which is the U.S. chronic water quality criterion
(US EPA, 1998).

Figure 1. Solubility of various metal sulfides and hydroxides.

Solubility of Metal Sulfides



Solubility of Metal Hydroxides in Pure Water (pH = 7)

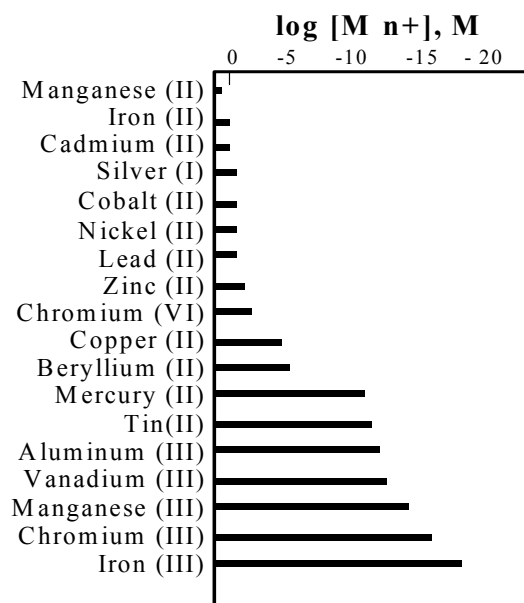


Figure 2. Observed and modeled release of radioisotopes from water column during days 1-21 in enclosures C-1 and C-2 (Diamond et al., 1990)

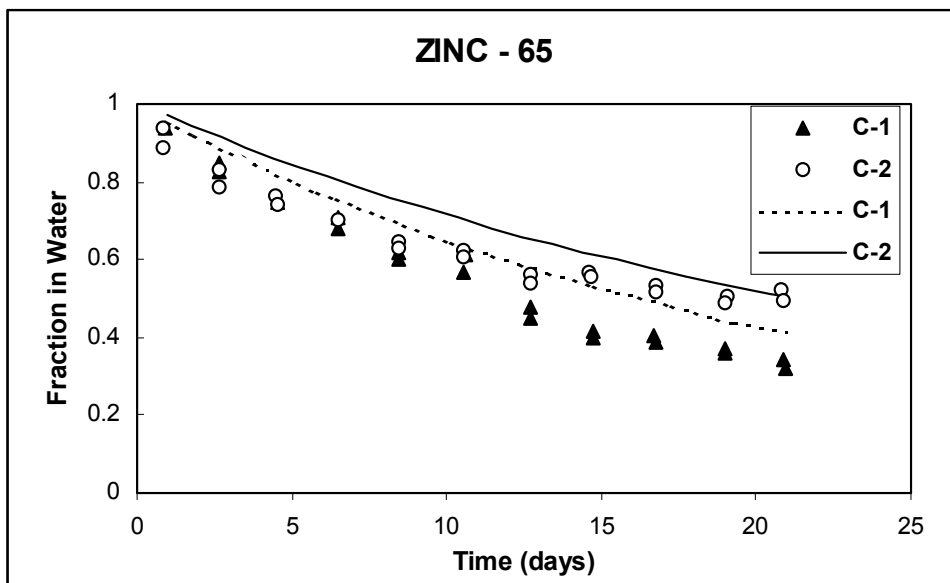
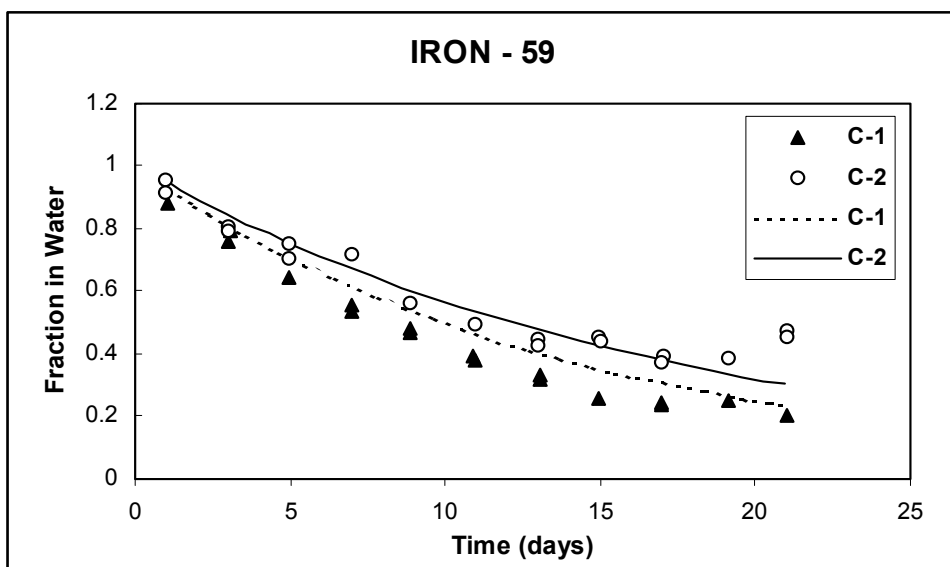
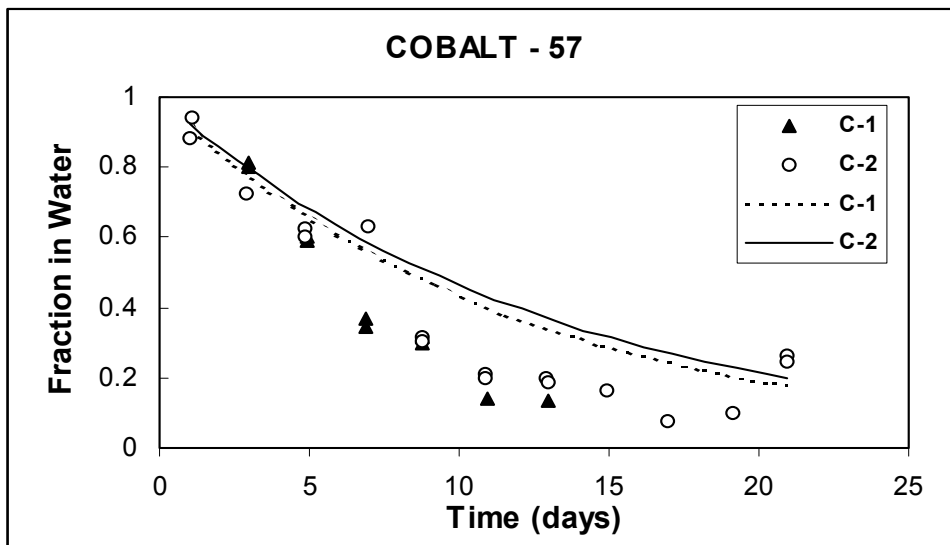


Figure 3. Half life versus particulate fraction. (A) Diamond et al., 1990
(B) MERL and EPS mesocosms (Adler et al., 1980)

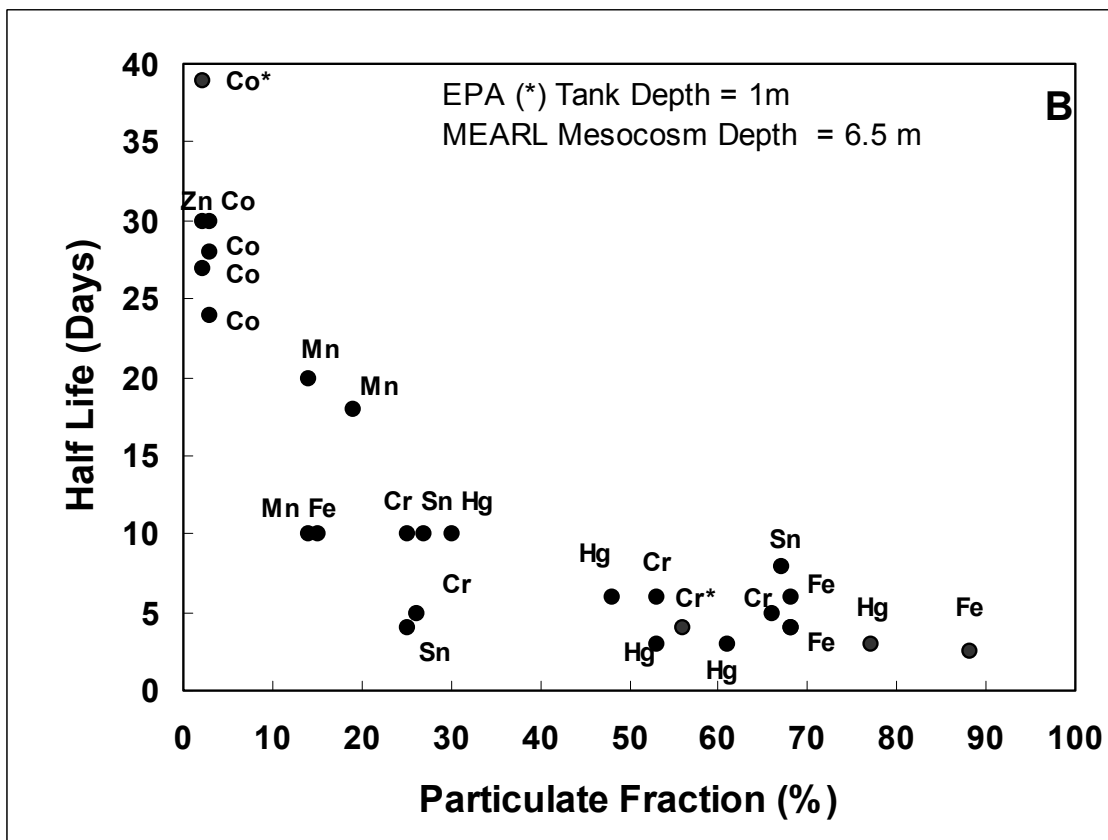
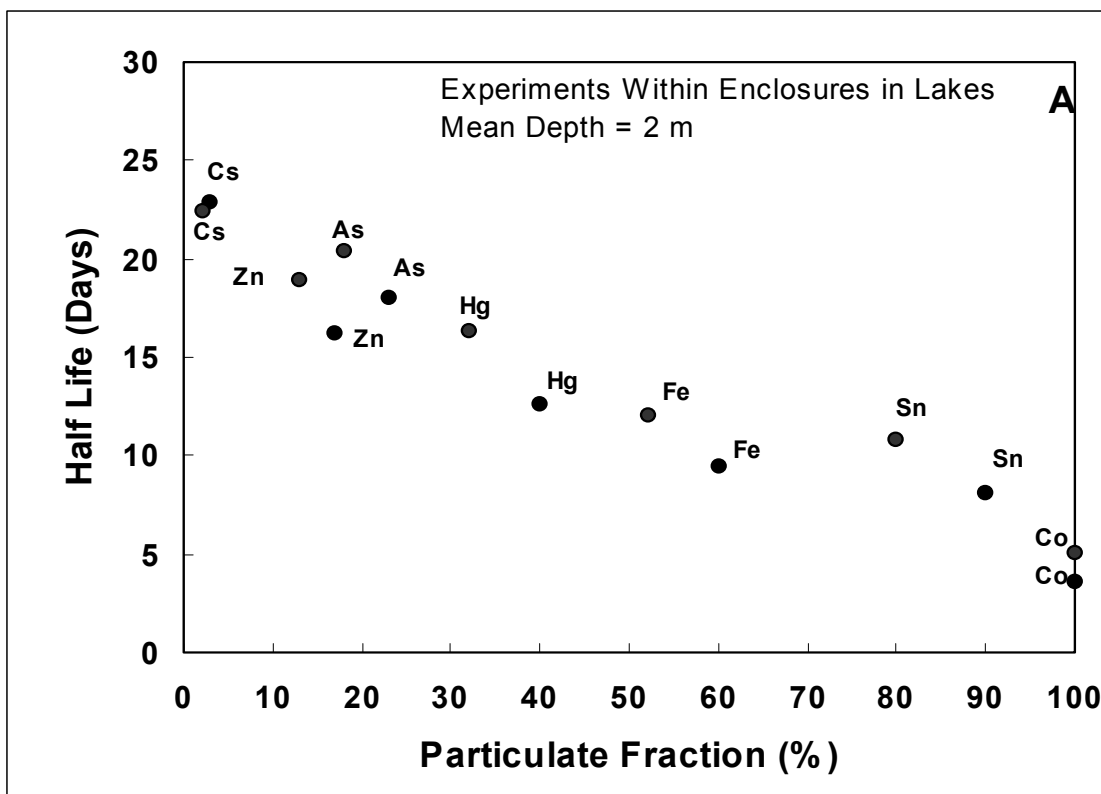


Figure 4. Observed MELIMEX concentrations (symbols connected with lines). Computed concentrations assuming no removal ($K=0$) and with removal ($K>0$). Equilibrium concentration also listed (Gachter, 1979)

Figure 5. Lake 224 in the Experimental lakes Area. Semi-logarithmic plots of total concentrations of metals versus time after addition to the lake (Hesslein and Broecker, 1980)

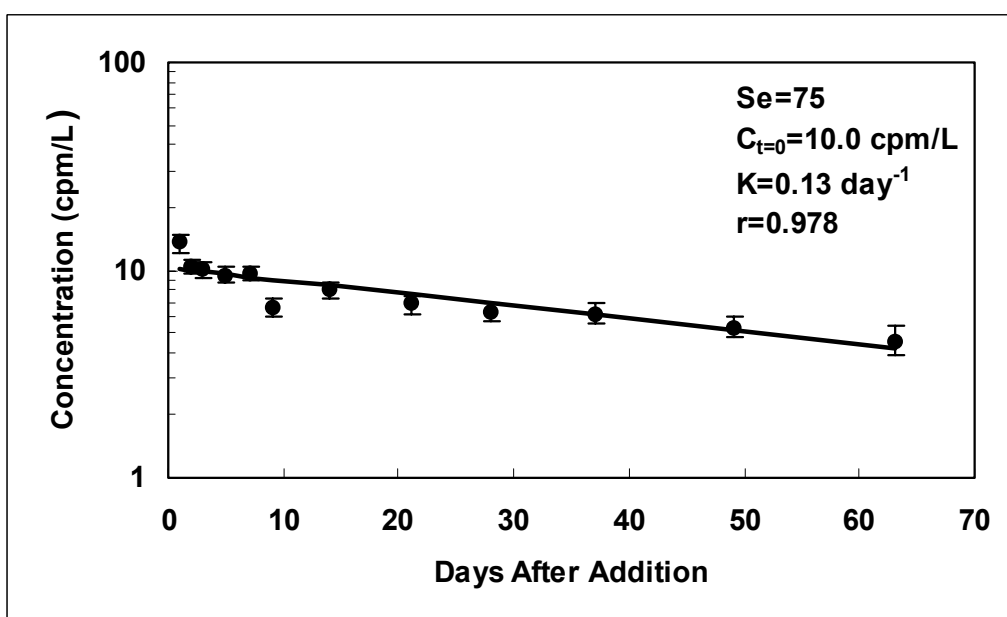
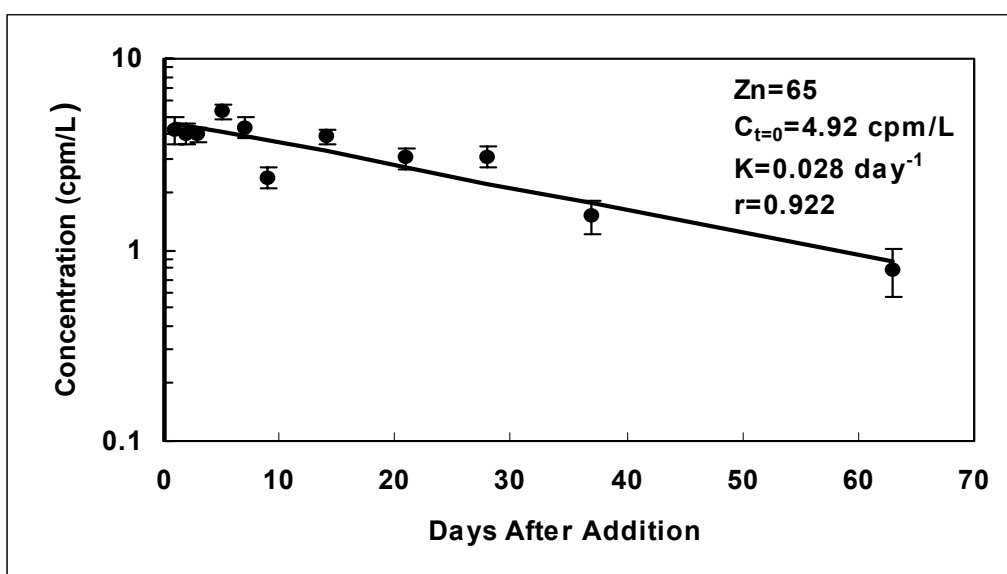
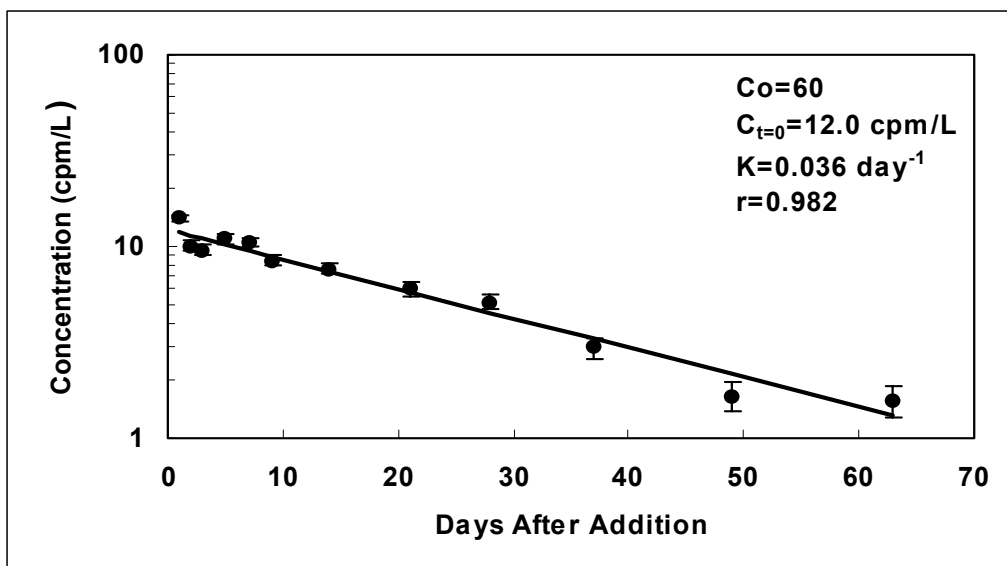


Figure 6. Half life versus particulate fraction (Hesslein and Broecker, 1980 and Effler et al., 1980)

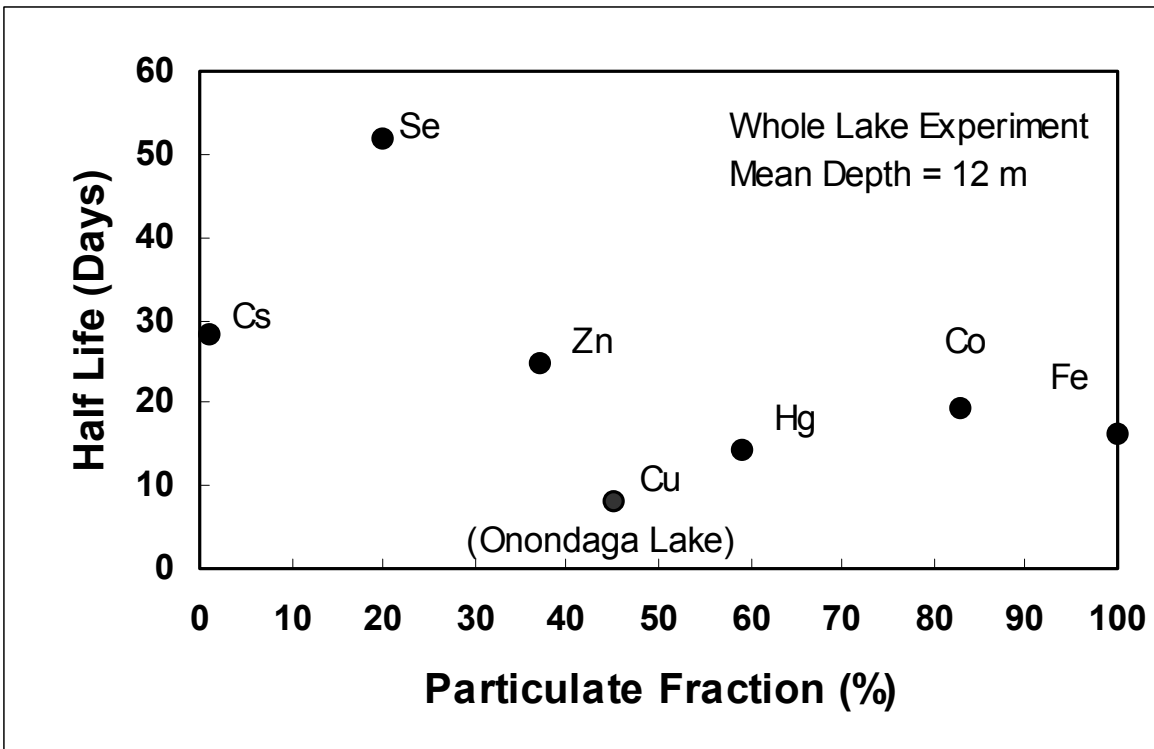


Figure 7. Metal regulation showing ranges of deficiency, homeostasis and toxicity.

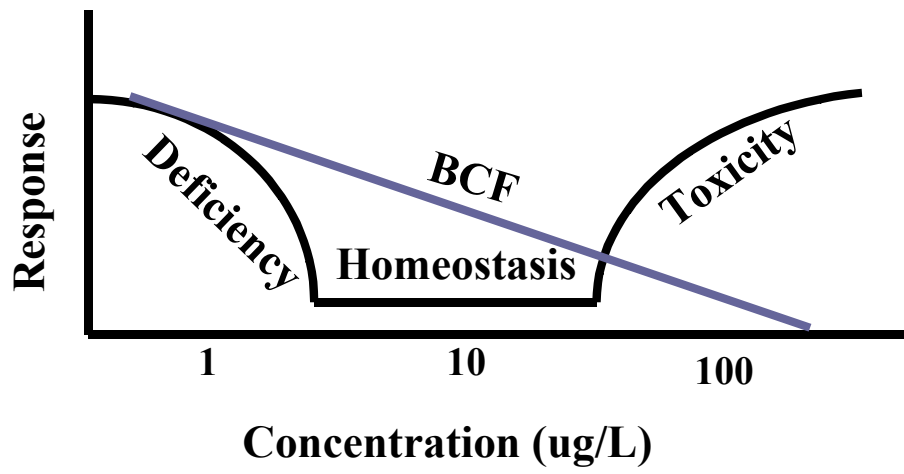


Figure 8. Zinc BCFs for Invertebrates

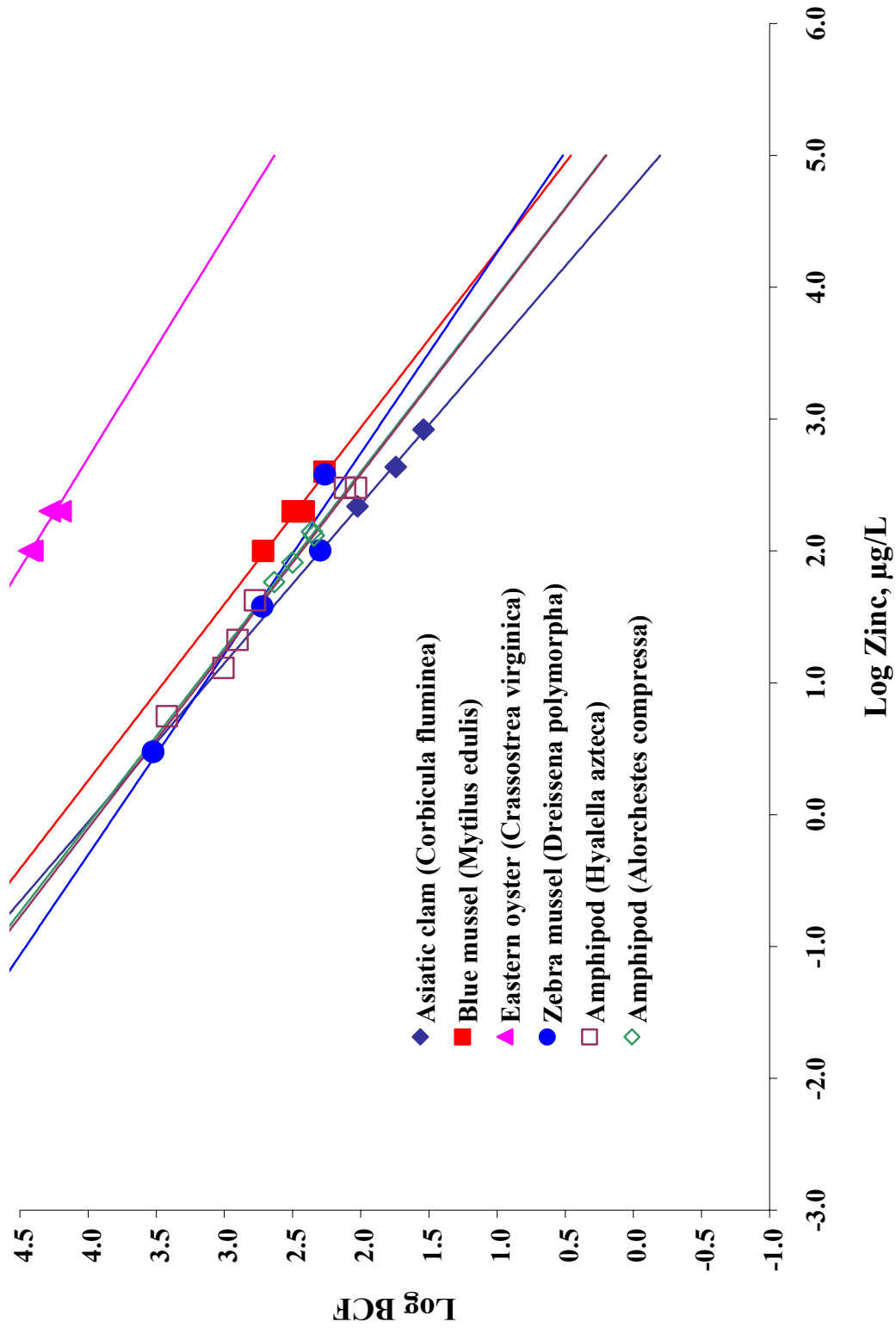


Figure 9. Cadmium BCFs for Non-Bivalve Invertebrates.

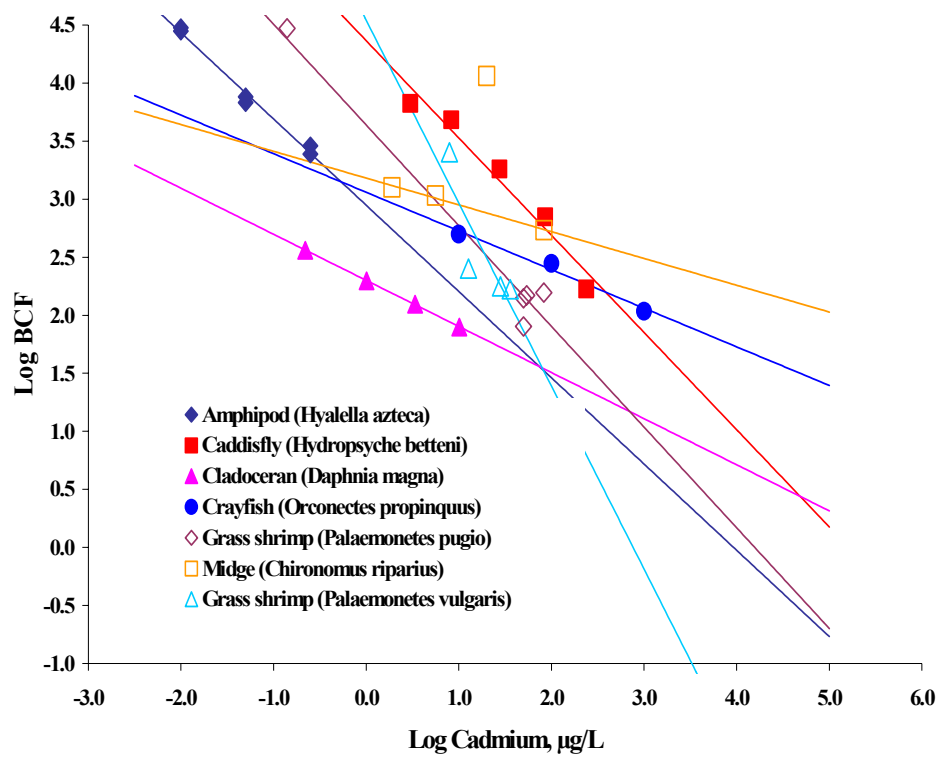


Figure 10. Relationship Between Cadmium BCFs for Daphnids and Insects

